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(54) COATING PROCESS FOR PROTECTING METALS OR METAL ALLOYS FROM CORROSION

(71) We, GESELLSCHAFT FÜR ELEKTROCHEMISCHE MATERIALBESCHICHTUNG MIT BESCHRÄNKTER HAFTUNG, Trading as ECM GESELLSCHAFT FÜR ELEKTROCHEMISCHE MATERIALBESCHICHTUNG MBH & Co. KG of 14 Reuterweg, Frankfurt-on-the-Main, Germany, a body corporate organised under the Laws of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for protecting metals or metal alloys from corrosion and/or for improving the adhesion of such metals or metal alloys for a lacquer coating or a deposited coating of plastics material.

Processes have been proposed for protecting metals or metal alloys from corrosive action by the application of a substantially organic coating, usually of lacquer or plastics material. Such a coating may also serve as a primer for a preferably decorative coating consisting of lacquer or a deposited plastics material. Based on mechanical application methods, processes have recently been developed in which deposition is effected under electrochemical action (electrophoretic lacquering, anodic or cathodic deposition of plastic material) and various proposals have been made for solving the specific problems encountered in this connection.

As the present invention also involves the production of a substantially organic coating, it is technologically related to some extent to the processes which have been outlined above. On the other hand, the present invention is not directed to the deposition of synthetic resins or plastics material.

According to the present invention there is provided a process for protecting a metal or metal alloy from corrosion and/or for improving the adhesion of said metal or alloy for a lacquer coating or deposited coating of plastics material, wherein the metal or metal alloy is connected to act as an anode or cathode and disposed in an aqueous bath which contains one or more surfactants, and wherein an electric current is passed though the bath to result in the formation on the metal or alloy of a coating consisting substantially of surfactant material, which coating is subsequently subjected to a heat treatment.

The subsequent heat treatment, is preferably carried out at a temperature within the range of 80 to 200°C.

Ionogenic surfactants, i.e., surfactants which are anionic or cationic, are particularly suitable for electrochemical deposition. Suitable surfactants include:

a) *Anionic surfactants*:
Fatty acid condensation products,
salts of alkyl sulphosuccinates,
salts of sulphonated castor oil hemiesters (Turkey-red oils),
alkyl sulphates,
alkyl phosphates,
alkyl sulphonates,
akyl aryl sulphonates;

b) *Cationic surfactants*:
N-alkylpyridinium salts,
alkylammonium salts,

c) *Non-ionic surfactants*:
Polyoxyalkylene adducts.

The surfactant concentration is preferably in the range of 1 to 100 grams per litre.

The pH-value is preferably in the range of 3 to 14. In the treatment of iron, it is preferably above 8, and in the treatment of aluminium, magnesium or alloys thereof in the range of 6 to 14.

Various reactions may be responsible for the formation of the water-insoluble coating, however, the formation of the insoluble coating is ensured by the subsequent heat treatment (stoving process).

In another alternative embodiment of the present process, an insoluble layer may be formed by a deposition of cationic and anionic surfactants in succession. The deposition may

[*Price 25p*]

be effected by cathodic and anodic actions, or this order may be inverted. In a modification of this embodiment, the first surfactant may be deposited on the metal or metal alloy by cathodic or anodic action and the second surfactant having an opposite charge may be applied by a non-electrochemical after-treatment to form the insoluble compound.

The electrochemical coating treatment is effected with the aid of direct current, alternating current or modulated direct current. The voltages required for a deposition lie generally between 2 and 250 volts, and in certain exceptional cases are up to 600 volts. The initial current density is preferably adjusted to be within the range of 0.05 to 20 amperes per square decimetre, and in exceptional cases, up to 80 amperes per square decimetre. The deposition time is between 2 and 60 seconds as a rule.

For a uniform formation of the layer, it is desirable to agitate the bath liquid and/or to move the articles to be treated.

The bath to be used in the present process preferably contains an addition of a complexing agent which can form complex ions with metal ions which go into solution. It has also proved desirable to use a bath which contains compounds adapted to suppress the discharge of oxygen or hydrogen on the articles to be coated. Such compounds are termed oxygen acceptors and hydrogen acceptors as they are capable of chemically binding gaseous oxygen and hydrogen, respectively, and thereby are themselves modified. An example of an oxygen acceptor is hydrazine which reacts with gaseous oxygen produced by the anodic action. An example of a hydrogen acceptor is hydrogen peroxide which reacts with gaseous hydrogen, produced by the cathodic action.

In the formation of coatings on aluminium, magnesium or their alloys, the sodium salt of sulphonated castor oil (Turkey-red oil) as an anionic surfactant and octadecyl-oxy-methylene-pyridinium chloride as a cationic surfactant have proved particularly suitable.

The addition of a fluoride, such as potassium fluoride, and the adjustment to a pH-value in a range of 6 to 14, result in additional improvements.

In the present process, minor quantities of organic organometallic or inorganic substances having a low or high molecular weight may be incorporated together with the surfactants. Examples of such substances are oils, fats, waxes, plastics materials and pigments. This modification of the process is possible because the surfactants have a very good wetting power on foreign matter and can suspend the same and compel it to migrate within an electric field.

The formation of a coating on metals or metal alloys by cathodic or anodic action may involve a strong generation of heat, by which the appearance and density of the coating will be affected. The generation of heat may cause, e.g., the formation of a layer which has an appearance like a lacquer.

When organic, organometallic or inorganic compounds are also used in the layer, the smoothness of the latter may be increased by an addition of flow-promoting or levelling agents and/or plasticizers.

The present process permits coatings having a high resistance to corrosion to be formed. The coatings also constitute an excellent primer for coatings or plastics material, which may be applied by conventional methods, e.g., by mechanical or electrochemical methods.

The invention will now be illustrated by the following non-limiting Examples.

In the following Examples, sheet metal panels having a size of 100 mm. × 100 mm. × 1 mm. were used and consisted of:

Iron containing 0.05% carbon; or
aluminium of grade 99.7 (soft).

As a pretreatment for the electrochemical coating with surfactants, the panels were first cathodically degreased in a bath composed of

sodium hydroxide	15 grams per litre
sodium carbonate	5 grams per litre
sodium cyanide	5 grams per litre
balance water.	

The process data for the cathodic degreasing were:

Voltage	10 volts
Current density	8 amperes per square decimetre
Degreasing time	60 seconds
Bath temperature	20°C.
Bath volume	2 litres

Counterelectrode (anode) stainless steel.

The degreased panels were rinsed with water.

The electrochemical coating was applied under the conditions stated in the following table.

Of the Examples:—

Example 1 comprises the coating of aluminium by anodic action with the sodium salt of sulphonated castor oil (Turkey-red oil), which is an anionic surfactant;

Example 2 comprises the anodic deposition of a higher alkylphosphoric acid ester, an anionic surfactant, on iron. The bath also contains hydrazine as an oxygen acceptor;

Example 3 comprises the cathodic deposition of a cationic fatty acid condensation product on iron;

Example 4 comprises the coating of iron. An aqueous bath is used, which contains a non-ionic surfactant consisting of a condensation. product of polyoxyethylene and polyoxypropylene, the bath also containing hydrazine as an oxygen acceptor;

Example 5 comprises the deposition of surfactants on aluminium in two stages. The first stage comprises the anodic deposition of anionic disodium octadecylsulphosuccinate. The subsequent second stage comprises the cathodic deposition of octadecyloxymethylenepyridiniumchloride, which is a cationic surfactant;

Example 6 also comprises a two-stage coating process. The first stage comprises the deposition of anionic disodiumoctadecylsulphosuccinate under the action of electric current. The second stage comprises a non-electrochemical treatment with a bath which contains cationic octadecyloxymethylenepyridiniumchloride.

TABLE

	Example 1	Example 2	Example 3
Coating on	aluminium	iron	iron
Type of coating treatment	anodic	anodic	cathodic
Surfactant	A	B	C
Type of surfactant	anionic	anionic	cationic
Concentration of surfactant (g./l.)	50	50	50
Additions to bath	K_2F_2, 6 g./l.	hydrazine, 18 g./l., NaOH 2 g./l.	—
pH-value of bath	8±2	12±2	6±1
Conductivity of bath, microsiemens-cm.$^{-1}$*	12,000	15,000	12000
Bath temperature, °C.	15—40	15—40	15—20
Operating voltage, volts	50	25	50
Initial current density, amperes per square decimetre	8	5	5
Coating time, seconds	5	15	10
Stoving temperature, °C.	120	160	160
Stoving time, minutes	5	10	10
Thickness of layer, nicrons	6—8	3—5	5—6

*1 Siemen = $1\Omega^{-1}$

	Example 4	Example 5	Example 6
Coating on	iron	aluminium	aluminium
Type of coating treatment	anodic	anodic-cathodic	anodic
Surfactant	D	Stage 1: E Stage 2: F	Stage 1: E Stage 2: F
Type of surfactant	non-ionic	E: anionic F: cationic	E: anionic F: cationic
Concentration of surfactant (g./l.)	50	Stage 1: 50 Stage 2: 50	Stage 1: 50 Stage 2: 100
Additions to bath	hydrazine, 18g./l., NaOH, 2g./l.	—	—
pH-value of bath	12±1	7±1	7±1
Conductivity of bath, microsiemens-cm.$^{-1}$	13,000	12,000	12,000
Bath temperature, °C.	15—40	15—40	15—40
Operating voltage, volts	100	2 × 50	E: 50; F: 0
Initial current density, amperes per square decimetre	1	5	E: 5; F: 0
Coating time, seconds	5	5	E: 5; F: 3
Stoving temperature, °C.	160	160	160
Stoving time, minutes	10	10	10
Thickness of layer, microns	2—3	8—10	6—8

A = Sodium salt of Turkey-red oil
B = alkyl phosphate
C = fatty acid condensation product
D = polyoxyethylene - polyoxypropylene adduct
E = disodiumoctadocylsulphosuccinate
F = octadecyloxymethylenepyridinium-chloride.

The described tests resulted in the formation of coatings which had a high bond strength and were uniform and cohesive and afforded an excellent protection against corrosion.

WHAT WE CLAIM IS:—

1. A process for protecting a metal or metal alloy from corrosion and/or for improving the adhesion of said metal or alloy for a lacquer coating or deposited coating of plastics material, wherein the metal or metal alloy is connected to act as an anode or cathode and disposed in an aqueous bath which contains one or more surfactants, and wherein an electric current is passed through the bath to result in the formation on the metal or alloy of a coating consisting substantially of surfactant material, which coating is subsequently subjected to a heat treatment.

2. A process as claimed in Claim 1, wherein the subsequent heat-treatment is carried out at a temperature in the range of 80 to 200°C.

3. A process as claimed in Claim 1 or 2, wherein the aqueous bath contains surfactant material in an amount of 1 to 100 grams per litre.

4. A process as claimed in any preceding Claim, wherein a complexing agent is added to the bath.

5. A process as claimed in any preceding Claim, wherein, when the coating is applied by anodic action, an oxygen acceptor is added to the bath.

6. A process as claimed in any one of Claims 1 to 4, wherein, when the coating is applied by cathodic action, a hydrogen acceptor is added to the bath.

7. A process as claimed in any one of Claims 1 to 5, wherein the coating is applied to aluminium, magnesium or an alloy thereof and the deposition is effected from an aqueous bath which contains the sodium salt of Turkey red oil.

8. A process as claimed in any one of Claims 1 to 4 and 6, wherein the coating is applied to aluminium, magnesium or an alloy thereof and the deposition is effected from an aqueous bath which contains octadecyloxymethylene-pyridiniumchloride.

9. A process as claimed in Claim 7 or 8, wherein potassium fluoride is added to the aqueous bath and the pH-value is adjusted to 6 to 14.

10. A process as claimed in any one of Claims 1 to 6, wherein the coating is applied in an aqueous bath which contains one or more ionic surfactants.

11. A process as claimed in any preceding Claim, wherein the coating is formed in two stages by treatment with a cationic surfactant and a subsequent treatment with an anionic surfactant.

12. A process as claimed in any one of Claims 1 to 10, wherein the coating is formed in two stages by treatment with an anionic surfactant and a subsequent treatment with a cationic surfactant.

13. A modification of the process claimed in Claim 11 or 12, wherein the treatment in the second stage is non-electrochemical.

14. A process for protecting a metal or metal alloy from corrosion and/or for improving the adhesion of said metal or alloy for a lacquer coating or deposited coating of plastics material as hereinbefore described in any one of the foregoing Examples.

15. A metal or metal alloy treated by the process claimed in any preceding claim.

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